

and Ni(110) surfaces. The change in the work function with coverage $\Delta\phi$ can, with some reservations, be identified with a quantity proportional to the quantity of hydrogen adsorbed, and thus with the conventional isotherm equations as developed by Langmuir and later workers, and put on a sound theoretical basis by Fowler. (For a concise account see Ref. 2, pp. 825–838.)

The results of dynamic and equilibrium measurements on the Ni(111) and (100) surfaces were quite similar to each other. Isothermic heats were substantially constant between $\Delta\phi$ values that would correspond to fraction coverage θ between 0.2 or less and about 0.6 to 0.8. These results indicate that the surface can be considered uniform, over a wide range of coverage.

The rate of adsorption, which depends on the hydrogen pressure, can be characterized by a function of θ and other variables. The sticking coefficient s is conveniently written as the sticking coefficient of a bare surface s_0 multiplied by $f(\theta)$ which is unity at zero coverage and zero at $\theta = 1$, but otherwise unspecified. The rate of desorption can likewise be characterized by a function $g(\theta)$ which multiplies a rate constant δ that is independent of coverage.

Independent kinetic measurements lead Christmann *et al.*, to the conclusion that adsorption is first order and that $f(\theta) = 1 - \theta$ and that desorption of H atoms to form H_2 is bimolecular or $g(\theta) = \theta^2$. These assignments lead to an isotherm of the form $C^{-1}[\theta^2/(1 - \theta)] = p_{H_2}$, which is in reasonable agreement with the isotherm data.¹

The mechanisms for adsorption and desorption aduced do not form a balanced pair and therefore cannot constitute the basis for an equilibrium isotherm. (See Ref. 2, pp. 659–660.) Thus the functions $f(\theta)$ and $g(\theta)$ are not independent of each other, except at some distance from equilibrium.³ It is clear that in this simple case that the mechanism for adsorption requires two sites for H and is also bimolecular so that $f(\theta) = (1 - \theta)^2$.

This change in $f(\theta)$ gives as the adsorption isotherm the Langmuir equation for dissociative adsorption $\theta/(1 - \theta) = (p_{H_2}/C)^{1/2}$.⁴ This equation also fits the data adequately in the intermediate range. The isotherm equa-

tion used by Christmann *et al.*, and the Langmuir equation fit the data equally well because they differ very little except at high coverage where the isosteric heat is dropping and neither equation is applicable.

In the simple case above, when the energy of adsorption is constant, and interaction between H atoms can be neglected, the Langmuir equation is inescapable for the case of localized bonding, but what of more complex models? The introduction of nearest-neighbor interaction with an interaction measured by an energy-of-interaction parameter χ_1 was used by Langmuir and Fowler to work out the simplest theory of the surface critical phenomenon. In the Bragg-Williams approximation, the adatoms are still distributed at random, so that $f(\theta)$ still may be set equal to $(1 - \theta)^2$. The isotherm has the form, (valid for very small values of χ_1/kT only)

$$p_{H_2}/C = [\theta/(1 - \theta)]^2 \exp[-2\theta\chi_1/kT].$$

Thus $g(\theta)$, in addition to the factor θ^2 contains an exponential term, which still implies a bimolecular process but with an (average) activation energy that varies (slightly) with coverage.

For the case where there is strong attractive interaction with 2D phase separation as is observed on the Ni(110) face, condensation and evaporation only along a line between the phases is an adequate balanced mechanism, even if one that is not realistic. This mechanism would suggest a zeroth order rate, rather than the first order evaporation rate observed by Christmann *et al.* Further analysis is suggested. Regions of intermediate interaction with incipient segregation are extremely difficult to discuss, even in the equilibrium state.

I am indebted to Professor S. Fain for valuable discussions.

¹K. Christmann, O. Schober, G. Ertl, and M. Neumann, *J. Chem. Phys.* 60, 4528 (1974).

²R. H. Fowler, *Statistical Mechanics*, (Cambridge University, Cambridge, England, 1936).

³L. Onsager, *Phys. Rev.* 37, 405 (1931).

⁴I. Langmuir, *Proc. Nat. Acad. Sci.* 3, 141 (1916); *J. Am. Chem. Soc.* 54, 2798 (1932).

Hydrodynamic boundary conditions and polymer dynamics*

Peter G. Wolynes and J. M. Deutch

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139
(Received 14 May 1976)

It is usual in polymer dynamics to picture a polymer chain as a connected sequence of segments immersed in a viscous medium. Kirkwood-Riseman (K/R) theory¹ treats these segments hydrodynamically as point centers of friction. In extending K/R theory, many authors have attempted to take into account the finite size of the segments.² In this note we focus on qualitative aspects of treating the segments as extended bodies and on the

role of hydrodynamic boundary conditions.

The dynamics of a polymer chain are described by a diffusion equation for the configuration probability distribution $P(\{\mathbf{R}_N\}, t)$

$$\frac{\partial P}{\partial t} = \sum_{j,k} \nabla_j \cdot \mathbf{D}_{jk} \cdot [\nabla_k P - (k_B T)^{-1} (\nabla_k U) P], \quad (1)$$

where summations run over the N segments of the chain,

$U(\{R_{Nj}\})$ is the interaction potential, and \mathbf{D}_{jk} the many-particle diffusion tensor, which is proportional to the inverse of the many-particle friction tensor $\mathbf{D}_{jk} = k_B T \times (\zeta)_{jk}^{-1}$.

In K/R theory the diffusion tensor is approximated by

$$\mathbf{D}_{jk} = k_B T [\zeta_0^{-1} \delta_{jk} \mathbf{I} + (1 - \delta_{jk}) \mathbf{T}(\mathbf{R}_{jk})] , \quad (2)$$

where ζ_0 is the friction coefficient for an individual segment and $\mathbf{T}(\mathbf{R})$ is the Oseen tensor

$$\mathbf{T}(\mathbf{R}) = \frac{1}{8\pi\eta_0 R} \left[\mathbf{I} + \frac{\mathbf{R}\mathbf{R}}{R^2} \right] , \quad (3)$$

which approximately describes the velocity perturbation induced at point \mathbf{R} due to a force exerted at the origin on an incompressible fluid of viscosity η_0 .

While asymptotically exact when the segments are so far apart as to be treated as point centers of force, the Oseen tensor is a severe approximation to the hydrodynamic interaction that would exist between two spherical beads of finite radius " a ". For neighboring segments a question arises about the consequences of an improved description of the interaction between the segments. At first glance the answer to this question is not reassuring. While it is not possible to solve exactly for the flow profile around all segments, it is possible to examine the case of radial motion of two segments. This should capture the essential limiting features since, when two segments come together and deviate strongly from the Oseen description, the presence of the other segments will not be crucial. In the case of relative radial motion, the strongest deviation from the Oseen approximation occurs. This motion, which arises in the nonsteady motion of the polymer, is described by a reduced diffusion equation.

$$\frac{\partial P_{rel}}{\partial t} = \nabla_r \cdot \left\{ \frac{2k_B T}{\zeta_0 \beta(r)} [\nabla_r P_{rel} - (\nabla_r U) P_{rel}] \right\} , \quad (4)$$

where we have used Eq. (2) for the case of the relative diffusion constant and write for the relative friction coefficient $(\zeta_0/2)\beta(r)$. According to the conventional wisdom one adopts *stick boundary conditions* on each segment; we may then use the exact series solution³ for $\beta(r)$. At large separations the limiting form for stick $\beta(r) - 1 + (3a/2r)$ is in agreement with Eqs. (2) and (3) when the stick expression for the segment friction coefficient is employed, $\zeta_0 = 6\pi\eta_0 a$. In contrast, at small separations, the exact expression for $\beta(r)$ diverges strongly as the spheres approach contact: $\beta(r) \sim a/[2(r - 2a)]$. This divergence is due to the large velocity gradients which arise between the segments. The deviations between the large separation limiting form, which in the Oseen approximation is assumed to hold at all separations, and the exact expression become progressively larger near contact and one might anticipate large deviations from the predictions of conventional polymer dynamics as are seen, for example, in the theory of diffusion controlled reactions.⁴

It is tempting to inquire if this situation would be substantially altered if one assumed *slip boundary conditions* in place of stick for each segment. The use of slip boundary conditions when hydrodynamics is applied

at the molecular level has recently been receiving a good deal of experimental support.⁵ In the context of conventional K/R theory, with the Oseen approximation, the net effect is to replace the stick value by the slip value $\zeta_0 = 4\pi\eta_0 a$ in Eq. (2). Such a scale change can be accommodated without discomfort. On the other hand, the resulting situation, when one examines corrections to the large separation Oseen approximation, is a good deal more reassuring. For a pair of spheres the results of Wacholder and Weihs⁶ for slip boundary conditions show at small separations $\beta(r) \sim \ln(r - 2a)^{-1}$, which is a much weaker divergence than the stick case. The divergence is sufficiently weak to give a finite coagulation rate in contrast to the stick case.⁷ Despite the logarithmic singularity, the difference between the exact $\beta(R)$ for slip and the large separation Oseen form $\beta(R) = [1 + (a/r)]$ is so slight that one may plausibly believe that the Oseen approximation is not too severe.

The differences between stick and slip boundary conditions are not as pronounced in the *steady flow* frictional properties of polymers. The translational friction constant, for example, does not involve the relative motion of the segments. For translation of two spheres along their line of centers, the exact result⁸ for the drag on stick spheres is finite and differs from the Oseen approximation at contact by only 10%. The Wacholder and Weihs result for slip spheres is closer to the Oseen approximation, differing by only 5% at contact. While exact results for other steady flow frictional properties are not available, it is unlikely that strong differences between stick and slip will arise, in contrast to the case of internal dynamics.

In summary, in this note we raise the possibility that in polymer dynamics slip boundary conditions should be imposed at the segments. At the level of the Oseen approximation this modification requires little quantitative adjustment, but, perhaps, a qualitative change in our image of solvent flow through a polymer. We have presented a heuristic argument that large quantitative differences between "stick" and "slip" will emerge for descriptions of internal polymer motions that are more accurate than the Oseen description. In contrast with stick, the results of a more accurate theory with slip is apt to agree within a few percent with the results of the Oseen approximation with slip.

*Supported in part by a grant from the National Science Foundation.

¹H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1971).

²R. Zwanzig, J. Kiefer, and G. H. Weiss, *Proc. Natl. Acad. Sci. (U.S.)* **60**, 381 (1966); J. Rotne and S. Prager, *J. Chem. Phys.* **50**, 4831 (1969); H. Yamakawa, *Ann. Rev. Phys. Chem.* **25**, 179 (1974).

³H. Brenner, *Chem. Eng. Sci.* **16**, 242 (1961).

⁴E. P. Honig, G. J. Roeberson, and P. H. Wiersema, *J. Colloid Interface Sci.* **36**, 97 (1971).

⁵O. R. Bauer, J. I. Brauman, and R. Pecora, *J. Am. Chem. Soc.* **96**, 6840 (1974).

⁶E. Wacholder and D. Weihs, *Chem. Eng. Sci.* **27**, 1817 (1972).

⁷P. G. Wolynes and J. M. Deutch, *J. Chem. Phys.* **65**, 450 (1976).

⁸M. Stimson and G. B. Jeffery, *Proc. R. Soc. (London) Ser. A* **111**, 110 (1926).